Extruded Cornstarch–Glycerol–Polyvinyl Alcohol Blends: Mechanical Properties, Morphology, and Biodegradability

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Elongation properties of extruded cornstarch were improved by blending with glycerol. Further blending of starch–glycerol with polyvinyl alcohol (PVOH) resulted in significant improvements in both tensile strength (TS) and elongation at break. Samples of starch–glycerol without PVOH equilibrated at 50% relative humidity had a TS of 1.8 MPa and elongation of 113%, whereas those containing PVOH had a TS and elongation of 4 MPa and 150%, respectively. Dynamic mechanical analysis (DMA) of starch–glycerol–PVOH blends showed that decreases in glass transition temperatures (T_g values) were proportional to glycerol content. Scanning electron microscopy (SEM) of fractured surfaces revealed numerous cracks in starch–glycerol (80:20) samples. Cracks were absent in starch–glycerol (70:30) samples. In both blends, many starch granules were exposed at the surface. No exposed starch granules were visible in blends with added PVOH. Starch–glycerol samples incubated in compost lost up to 70% of their dry weight within 22 days. Addition of PVOH lowered both the rate and extent of biodegradation.

KEY WORDS: Extruded; polyvinyl alcohol; starch; glycerol; biodegradation; films.

INTRODUCTION

Over the past two decades, utilization of starch has become an extremely active research area within the United States Department of Agriculture (USDA), as well as within other institutions [1–3]. Starch, a renewable resource, is available in abundant quantities at a very low cost in the United States [4]. New uses for starch will enhance demand for farm commodities and create agribusiness jobs, thereby improving the position of the United States in the global marketplace, where more than $100 billion in trade deficits have become an economically threatening norm. Replacing plastic derived from imported petroleum, particularly that destined for single-use items, with starch-based materials will directly improve this trade imbalance. Furthermore, starch is highly biodegradable and, therefore, offers potential advantages over recalcitrant synthetic plastics in disposable applications.

Starch itself is very brittle and has poor mechanical properties for plastic applications. However, by blending

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with plasticizers, such as water, selected amino acids, or glycerol, elongation can be improved significantly, but tensile strength (TS) is negatively impacted [5–8]. The improvement in the mechanical behavior of a polymer from stiff/brittle to soft/flexible is due to increased molecular mobility at room temperature [8, 9]. Thus, the glass transition temperature (T_g) of starch can be affected by the presence of small molecular plasticizers, and changes in T_g have been investigated using a differential scanning calorimeter (DSC) and dynamic mechanical analysis (DMA) [10–13].

Efforts to overcome mechanical deficiencies of starch have also included blending with other polymers, such as polyethylene, polyhydroxyalkonates, polylactic acid, protein, pectin [14–18], and polyvinyl alcohol (PVOH) [6, 7]. Starch–PVOH blends represent one of the few commercial successes, and have been marketed as water-soluble laundry bags. However, although starch–PVOH films initially exhibit desirable properties, their quality deteriorates fairly rapidly with time.

Surprisingly few studies have been published that characterize starch–PVOH blends. Westhoff *et al.* [6] evaluated various polyols, including glycerol, as plasticizers for starch–PVOH cast films and noted a loss of methanol-extractable glycerol from aged films, as well as a loss of plasticizer effectiveness in films prepared with high starch loads. More recently, Lawton and Fanta [7] examined the effect of polyethylene-*co*-acrylic acid (EAA) on starch–glycerol–PVOH composites. This study utilized cast films as well and concluded that a small amount (ca. 3%) of EAA was optimum for obtaining films having at least 100% E and TS of 25 MPa, while maintaining starch content above 50%. Stenhouse et al. [19] utilized extruded, blown films of starch–glycerol–PVOH to examine, among other things, the effect of PVOH molecular weight on the physical properties of the film. One formulation which employed intermediate molecular weight PVOH appeared to be particularly attractive because it exhibited very low oxygen permeability in addition to acceptable mechanical properties. Unfortunately, as the authors noted, their results should be interpreted only qualitatively because neither sample storage nor tensile testing were accomplished under controlled humidity. Nevertheless, the promising results of that study prompted us to examine starch–glycerol–PVOH composites more thoroughly. In this study, the fractured surface as well as mechanical, thermal, and biodegradative properties of extruded starch–glycerol–PVOH formulation were evaluated.

EXPERIMENTAL

Materials

Unmodified commercial grade cornstarch (Buffalo 3401, 10.3% moisture) was obtained from CPC International Inc., Argo, IL. PVOH (Airvol 425) was purchased from Air Products and Chemicals Inc., Allentown, PA. Airvol 425 was 95.5–96.5% hydrolyzed with a molecular weight average of 100,000–146,000. Reagent grade glycerol was from Fisher Scientific, Pittsburgh, PA.

Material Processing and Extrusion

In samples without PVOH, starch (10.3% moisture) and glycerol (0.2% moisture) were mixed directly together with a Kitchenaid mixer for 10 min. Formulations contained 35, 32, 30, 25, 23, and 20% glycerol (weight basis) without any added water. Samples with PVOH were prepared as follows: Water was added to a predetermined amount of glycerol and the weight was adjusted to 45 g. The mixture was stirred at room temperature and, while being stirred, PVOH was added. The solution was heated to 85°C for 30 min. This preparation was then mixed with starch in the Kitchenaid mixer at room temperature (24°C). Formulations contained 10 g of PVOH (final concentration of 9.1%) and 100 g of starch, unless otherwise indicated, whereas glycerol contents varied from 0 to 35% (weight basis). All formulations were extruded through a single-screw extruder (model RC-0500, Randcastle Inc., Cedar Grove, NJ) equipped with a strand die. The temperatures for the die and zone 1, 2, and 3 were 121°, 135°, 129°, and 110°C, respectively. Screw speed was adjusted to 30 rpm.

Mechanical Testing

Dog-bone-shaped samples were stamp-cut from the extruded ribbons. Tensile properties were measured at 25°C using an Instron Universal Testing System (Instron Corp., Canton, MA). Dog-bone-shaped samples had a width of 3.9 mm and length of 25 mm in the neck. The thickness of test sample was measured three times along the neck and averaged. The cross-head speed was at 20 mm/min. Where indicated in the text, samples were equilibrated under controlled relative humidities of 30, 50, and 93% for 2 weeks.

Dynamic Mechanical Analyses (DMA)

The DMA instrument (DMA 7, Perkin-Elmer, Norwalk, CT) was used to measure storage modulus, loss modulus, and tan δ versus temperature of the extruded

sample. The relaxation temperatures were determined from the obtained plots. All samples were cut into small bars (20 × 3.9 mm) and conditioned at 50% relative humidity (RH) for 2 weeks. Tests were performed utilizing a three-point bending system at a frequency of 1 Hz and heating rate of 10°C/min. over a temperature range of −125 to 130°C.

Scanning Electron Microscopy (SEM)

SEM was used to examine the fracture surface of the extruded ribbon samples. Specimens were prepared following the method described elsewhere [20]. Specifically, samples were conditioned for a period of 48 h under 50% RH. Samples were quickly frozen at −32°C in dry ice and fractured with a sharp knife. Samples with fractured surfaces were mounted on aluminum stubs with graphite-filled tape and vacuum coated with gold–palladium. Samples were then examined using a model JSM 6400v scanning electron microscope (JEOL Inc., Peabody, MA).

Biodegradation Studies

Extruded starch ribbons with 20 and 30% glycerol or with 20% glycerol plus 9.1% PVOH were cut into 2 × 5 cm samples and were weighed. Samples were then layered in 7–10 cm thick compost (Lee County Recycling Center, Madison, IA) and were incubated for up to 22 days at 28°C. At indicated intervals, samples were recovered and weight losses were calculated.

The data provided in this manuscript represent duplicate samples from at least three experiments that were averaged together and had <5% variation.

RESULTS AND DISCUSSION

Starch–glycerol extruded specimens generally exhibited poor physical properties (TS, elongation) when equilibrated at high relative humidity (93% RH) prior to testing. Increasing glycerol content in the blend from 20 to 35% did not improve these properties (Fig. 1). In samples equilibrated at 50% RH, both TS and elongation were directly affected by glycerol content, albeit in a reversed manner. Highest TS (9.7 MPa) was achieved with 20% glycerol and any further increase in glycerol content had a negative effect. Conversely, elongation increased proportionally to 113 at 30% glycerol content, whereas further increase in glycerol had a negative effect on elongation. Shogren et al. [11] melt extruded starch with 40% glycerol (based on starch weight) and observed
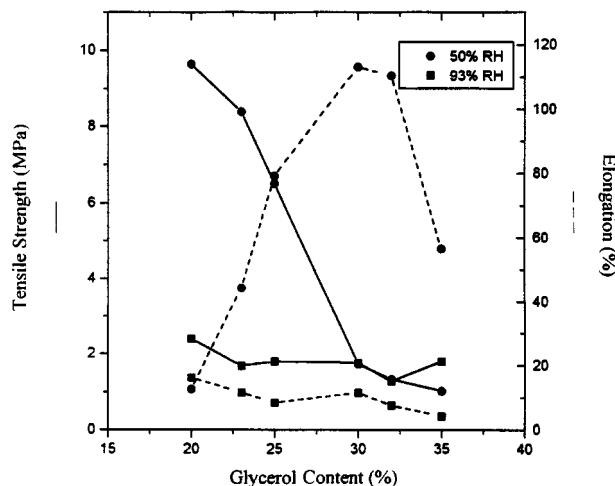

Fig. 1. Tensile strength (TS) and elongation at break of extruded starch–glycerol formulations of varied proportions.

TS values of about 1.5 MPa and elongation values of about 60% when samples were equilibrated at 50% RH. The data presented in Fig. 1 are in good agreement with these observations. Formulations equilibrated at 30% RH were too brittle to test.

Studies were conducted to investigate the effect of added PVOH on starch–glycerol blends. About 10 g PVOH was added to the various starch–glycerol blends and its impact on TS (Fig. 2) and elongation (Fig. 3) was evaluated. Overall physical properties were enhanced by
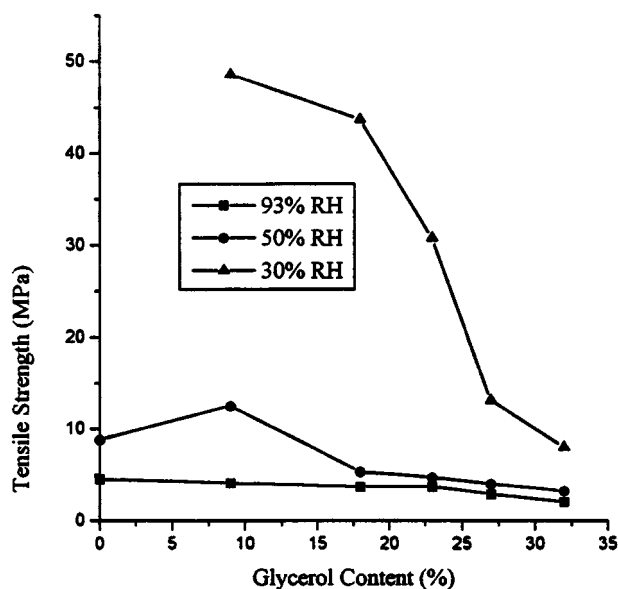

Fig. 2. Tensile strength (TS) of extruded starch–glycerol–PVOH formulation. PVOH content was constant at 10 g (9.1), while the proportions of starch and glycerol varied.
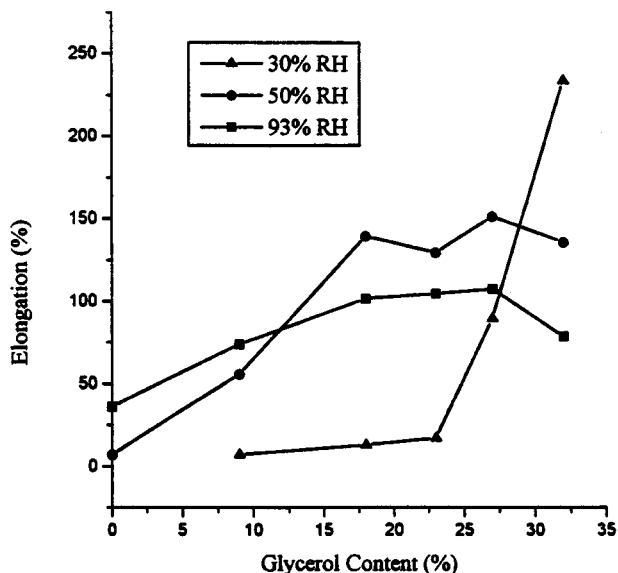
Fig. 3. Percent elongation (%*E*) of starch–glycerol–PVOH formulation. PVOH content was constant at 10 g (9.1), while the proportions of starch and glycerol varied.

addition of PVOH. For instance, at 30% glycerol content and 50% RH, the added PVOH increased TS to 4 from 1.8 MPa, and increased elongation to 150 from 113%. Addition of PVOH also made it possible to conduct physical property tests at 30% RH. Starch–glycerol–PVOH formulations were sensitive to RH. Specimens consistently exhibited higher TS at lower RH values (Fig. 2). Generally, elongation increased at higher RH values, with a notable exception at 35% glycerol content (Fig. 3). This concentration, starch–glycerol–PVOH ratio of 65:35:9 at low RH (30%), yielded the highest elongation value (230%) of the study. Starch–PVOH formulations without glycerol were extremely brittle at 30% RH, precluding physical testing.

The dynamic mechanical properties of pure PVOH and starch–glycerol (80:20) extruded samples equilibrated at 50% RH were investigated. The glass transition (T_g) temperatures were estimated from the storage modulus log E' and tan δ as a function of temperature (Fig. 4) following the method of Kalichevsky *et al.* [10]. Results indicated T_g values of 65°C for pure PVOH and 53°C for the starch–glycerol samples. The tan δ peak at −30°C in starch–glycerol samples was only observed when glycerol was present. This transition is probably due to secondary transition of starch, showing the plasticization effect of glycerol (Fig. 4).

Increased concentration of glycerol plasticizer from 0 to 35% in the starch–glycerol–PVOH formulation impacted material properties in that both tan δ and storage modulus decreased proportionally with increased glycerol

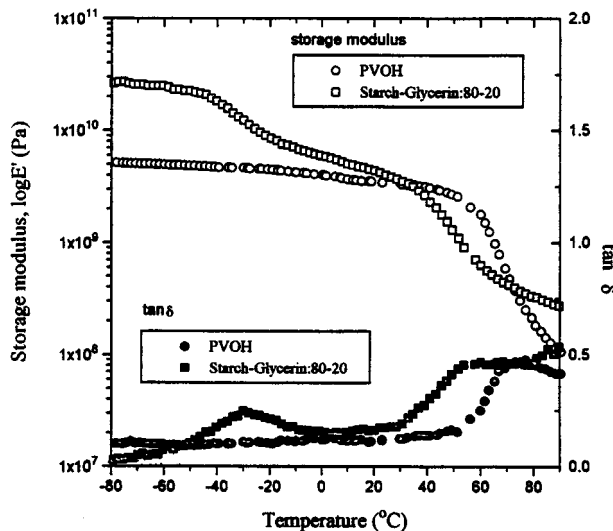**Fig. 4.** Temperature dependence of storage modulus and tan δ in pure PVOH and starch–glycerol samples.

content (Table I). As expected, decreased T_g values were also observed with increased glycerol content in samples.

The T_g of PVOH has been reported to be between 65° and 86°C, depending on the experimental method used and the amounts of residual acetate and moisture present in the samples [21]. Because water acts as a plasticizer, this could lead to somewhat lower T_g values for PVOH than seen in this study with pure PVOH. Using DSC methods, Shogren *et al.* [11] observed a T_g of 57°C for extruded starch–glycerin (89:11) material. Lourdin *et al.* [12] studied the T_g of potato starch blended with glycerol and found that the T_g obtained from DMA was always higher than the T_g obtained using DSC methods. This difference in T_g values from two methods may be because during DMA analysis, the test sample is heated in an open environment, allowing moisture to escape, hence increasing the T_g.

Table I. Dynamic Mechanical Analyses and Estimated T_g Values of Starch–Glycerol–PVOH Formulations

Starch–glycerol–PVOH ratio	$T_1{}^a$ (°C)	$T_2{}^b$ (°C)	T_g (estimated from E' and tan δ)
0–0–100	55	75	65
80–20–0	38	60	49
100–0–10	61	70	66
85–15–10	48	70	59
80–20–10	15	57	36
70–30–10	8	35	22
65–35–10	−4	6	5

a Temperature at the onset of drop of storage modulus (E').
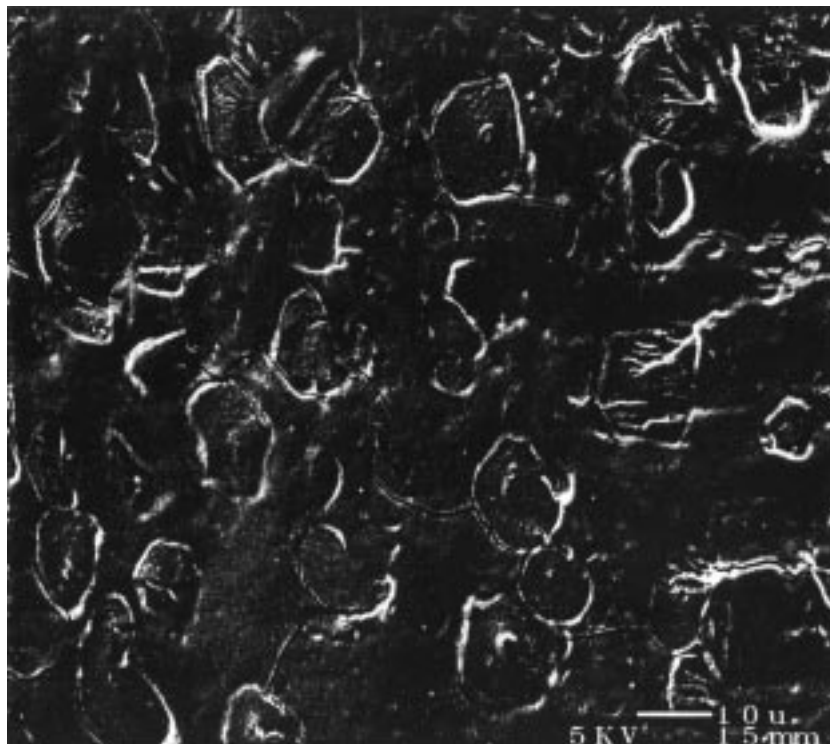*b* Temperature at the peak of strain/stress phase difference tan δ.

Fig. 5. SEM of fracture surface of starch–glycerol (80:20) formulation.

SEM of the fractured surfaces revealed exposed starch granules on the surface in blends containing 20 and 30% glycerol (Figs. 5 and 6). Starch blends with 20% glycerol had many apparent cracks throughout the surface (Fig. 5), whereas in samples with 30% glycerol, the surface appeared to be smooth without any cracks (Fig. 6). The fact that the blend with 20% glycerol was very brittle and had lower elongation compared to the blend with 30% glycerol may account for the appearance of such cracks. However, addition of PVOH in a starch blend with 20% glycerol not only improved physical properties of the blend, but under SEM the surface appeared to be smooth and uniform with no exposed starch granules (Fig. 7). In addition, PVOH also prevented the appearance of cracks noted in Fig. 5. The disappearance of starch granules on the surface may be due to the higher moisture content in this blend, which allowed more complete gelatinization or destructurization of granular starch during the extrusion process. In this regard, Zhiqiang *et al.* [22] reported that a 50:50 (weight basis) mixture of glycerol and water provides the best plasticizing properties for compounding starch, and that further incorporation of PVOH leads to enhanced mechanical properties and increased melt viscosity.

About 70% weight loss was observed in 20 and 30% starch–glycerol blends without PVOH within 22 days of exposure in compost (Fig. 8). The extent and rate of weight loss were quite similar for both formulations. The weight loss was only 59% in starch–glycerol formulations with added PVOH, suggesting that the addition of PVOH slowed the degradation process in these samples. In this regard, Chen *et al.* [23] observed that increased PVOH content in starch–PVOH cast films improved elongation properties, but the rate of biodegradation in these films was negatively correlated with the PVOH content.

CONCLUSIONS

Addition of PVOH in starch–glycerol blends significantly improved both the TS and elongation of the extruded materials. DMA analysis showed that T_g values in blends decreased with increased glycerol content. Addition of PVOH to starch–glycerol blends prevented the development of surface cracks and improved mechanical properties. As expected, the starch–glycerol extruded ribbons biodegraded rapidly in soil. Addition of PVOH to blends slowed the biodegradation process.
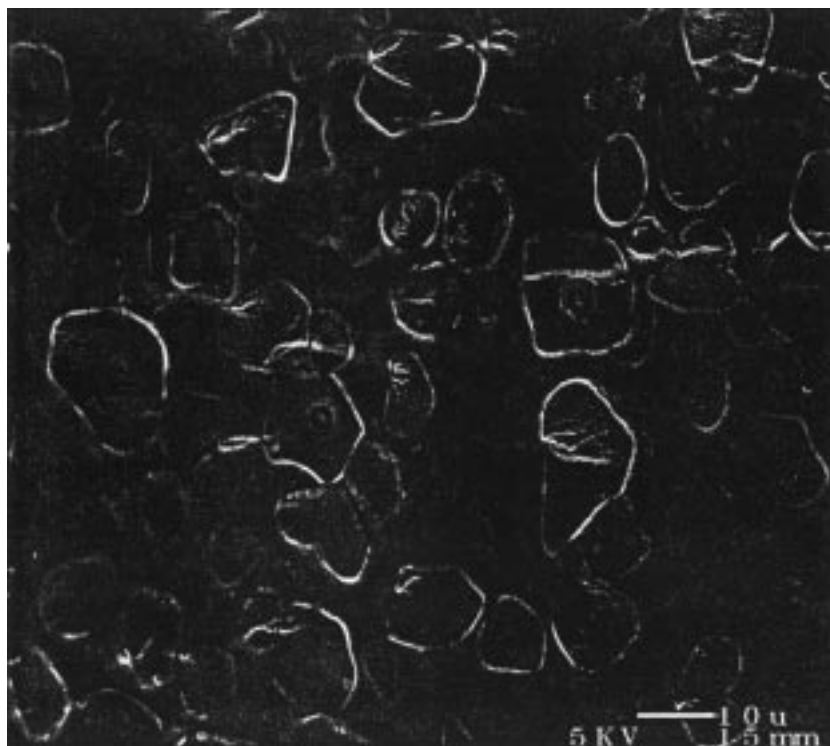
ACKNOWLEDGMENTS

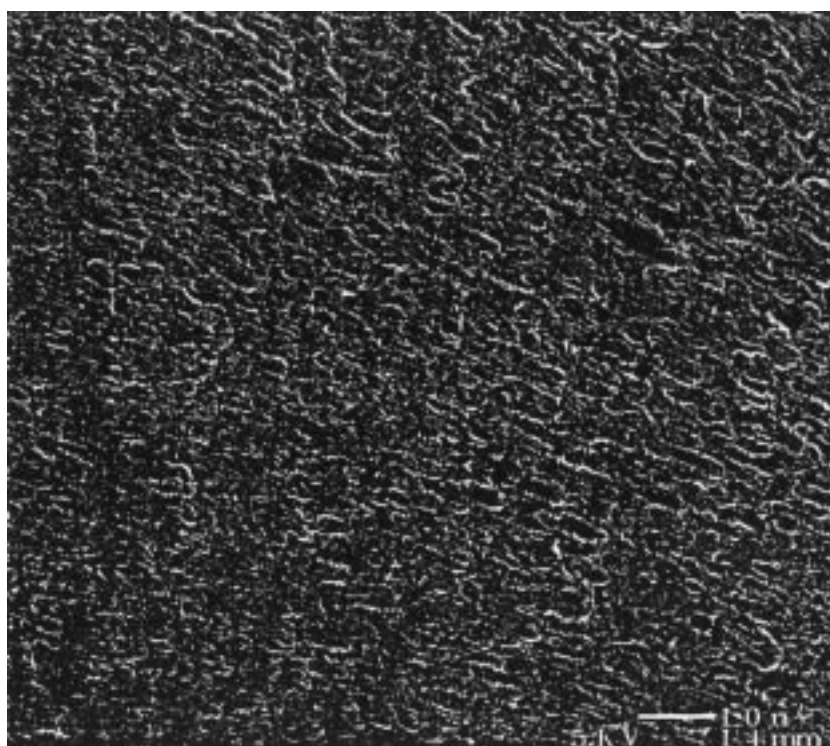**Fig. 6.** SEM of the fracture of starch–glycerol (70:30) formulation.

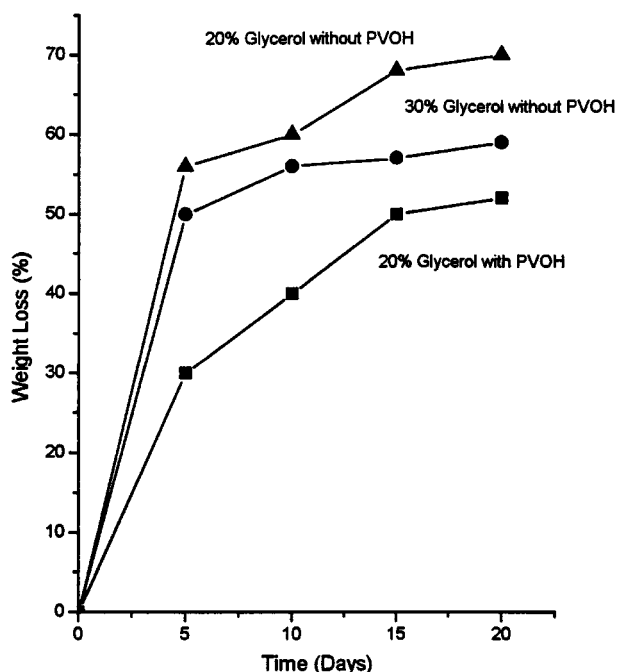**Fig. 7.** SEM of fracture surface of starch–glycerol–PVOH (80:20:10) formulation.

Fig. 8. Weight loss in starch–glycerol formulation with and without added PVOH in soil.

REFERENCES

1. C. L. Swanson, R. L. Shogren, G. F. Fanta, and S. H. Imam (1993) *J. Environm. Polym. Degrad.* **1,** 155–165.

2. W. M. Doane (1994) *J. Polym. Mater.* **11,** 229–237.
3. H. Roper and H. Koch (1990). *Starch/Störke* **42,** 123–130.
4. *Plastic News* (1992).
5. R. L. Shogren (1993) in *Biodegradable Polymer and Packaging*, C. Ching, D. L. Kaplan, and E. L. Thomas (Eds.), Technical Publishing Company, Lancaster, PA, Chapter 10, pp. 141–150.
6. R. P. Westhoff, W. F. Kwolek, and F. H. Otey (1979). *Starch* **31,** 163–165.
7. J. W. Lawton and G. F. Fanta (1994) *Carbohydr. Polym.* **23,** 275–280.
8. T. M. Stein and R. V. Greene (1997) *Starch/Störke* **49,** 245–149.
9. T. Alfrey (1948) *Mechanical Behavior of High Polymers*, Interscience Publishers, New York, pp. 581.
10. M. T. Kalichevsky, E. M. Jaroszkiewicz, S. Ablett, J. M. V. Blanshard, and P. J. Lillford (1992) *Carbohydr. Polym.* **18,** 77–88.
11. R. L. Shogren, C. L. Swanson, and A. R. Thompson (1992) *Starch* **44,** 335–338.
12. D. Lourdin, H. Bizot, and P. Colonna (1997) *J. Appl. Polym. Sci.* **63,** 1047–1053.
13. R. J. Nicholls, I. A. M. Appelqvist, A. P. Davies, S. J. Ingman, and P. J. Lillford (1995) *J. Cereal Sci.* **21,** 25–36.
14. N. St.-Pierre, B. D. Favis, B. A. Ramsey, J. A. Ramsey, and H. Verhoogt (1997) *Polymer* **38,** 647–655.
15. H. Verhoogt, N. St.-Pierre, F. S. Truchon, B. A. Ramsey, B. D. Favis, and J. A. Ramsey (1995) *Can. J. Microbiol.* **41** (suppl. 1), 323–328.
16. K. Mizuno (1996) JP 8245768 A2 24 Sept.
17. F. P. Matthey and M. A. Hanna (1997) *Food Sci. Technol.* **30,** 359–366.
18. M. L. Fishman, D. R. Coffin, J. J. Unruh, and T. Ly (1996) *J. Macromol. Sci. Pure Appl. Chem.* **A33,** 639–654.
19. P. J. Stenhouse, J. M. Mayer, M. J. Hepfinger, E. A. Costa, P. A. Dell, and D. L. Kaplan (1993) in *Biodegradable Polymer and Packaging*, C. Ching, D. L. Kaplan and E. L. Thomas (Eds.), Technical Publishing Company, Lancaster, PA, Chapter 11, pp. 151–158.
20. S. H. Imam, L. Chen, S. H. Gordon, R. L. Shogren, D. Weisleder, and R. V. Green (1998) *J. Environ. Polym. Degrad.* **6,** 91–98.
21. R. K. Yubbs and T. K. Wu (1973) *Polyvinyl Alcohol, Properties and Applications*, C. A. Finch (Ed.), Wiley-Interscience, New York, Chapter 8, pp. 167–181.
22. L. Zhiqiang, Y. Feng, and Y. Xiao-Su (1999) *J. Appl. Polym. Sci.* **74,** 2667–2673.
23. L. Chen, S. H. Imam, S. H. Gordon, and R. V. Greene (1997) *J. Environ. Polym. Degrad.* **5,** 111–117.